Conjugative interactions in dithienothiophene-dioxides

Jong, Feike de

SUMMARY

The present experimental and theoretical study was undertaken for the purpose of correlating the structure of dithienothiophene dioxides with their chemical and physical properties.

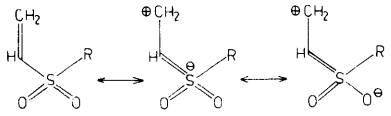
The parent compounds, the dithienothiophenes (1-6) have been synthesized using oxidative ring closure of the appropriate dilithio-dithienyl sulfides (ch. 2). The dilithio intermediates were obtained from α,α'-dibromodithienyl sulfides by halogen-metal interconversion. A new method is reported for the synthesis of symmetric dithienyl sulfides, consisting of the reaction of thienyllithium with bis(phenylsulfonyl)sulfide (8). The ultraviolet spectra of the dithienothiophenes are in excellent agreement with those calculated by SCF-MO methods (section 2.2).

Peracid oxidized exclusively the sulfur atom of the central ring of the dithienothiophenes. The corresponding dioxides were obtained in good yields using m-chloroperbenzoic acid in dichloromethane solution. The dithienothiophene-oxides could be prepared in low yields only by the reaction of the parent sulfur compound with m-chloroperbenzoic acid in methanol solution (ch. 3).

The interaction of the sulfone group and the adjacent dithienyl moiety has been treated on the basis of HMO theory (ch. 4). The sulfur atom of the SO_2 group is assumed to form π-bonds by means of its 3d-orbitals. The set of empirical parameters was chosen so as to fit the experimental electronic transition energies. Using this model for the sulfonyl moiety a good correlation has been obtained between the longest wavelength absorption band and the calculated $N \rightarrow V_1$ transition energy for a large number of sulfones. The longest wavelength absorption band can be considered as an intramolecular charge transfer band, with the sulfonyl group acting as the electron acceptor. This "donor-acceptor" type of resonance (structure Ib) does not affect the π-bonding between sulfur and oxygen (section 4.4.).

Furthermore, the polarographic half wave reduction potentials determined in anhydrous DMF showed a good correlation with the calculated energies of the lowest unoccupied MO (section 4.5.).

The contribution of "ketonic" type of resonance (
to the ground state of conjugated sulfones was calc



Ia Ib Ic

zero for Case II and small for Case I sulfones. Th
confirmed experimentally, since the S-O stretching
showed a small decrease upon going from Case II
sulfones (ch. 5).

The effect of "ketonic" type of resonance on the
bonding ability of sulfones could not be evaluated,
the dominating influences of other effects. Howeve
relationship between the S-O stretching frequencies
and the hydrogen bonding abilities can be used to
the presence of conjugative interactions (section 5.

From a comparison of calculated molecular quan
experimental data (collected from the literature),
containing the sulfonyl moiety, it is concluded that
π-electron effects are not (or only to a small exte
transmitted by the sulfur atom of the SO_2 group in
state of sulfonyl compounds (ch. 6). In contrast, i
effects are transmitted effectively. It is suggested
large influences of inductive effects may be due to
hybridization of the sulfur atom in sulfonyl compou